

ATTACHMENT 14A

Radioactive Decay and Equilibrium

The rate of decay of a number of atoms, N_1 , of a radionuclide can be expressed by Equation 14A.1, where λ_1 is $(\ln 2)/t_{1/2}$ for the radionuclide and t is the time during which the change in N_1 is observed:

$$-\left(\frac{dN_1}{dt}\right) = \lambda_1 N_1 \quad (14A.1)$$

The radionuclide may decay to a stable nuclide, or to another radionuclide. In the first instance, the total number of atoms of stable nuclide formed as a result of the decay of N_1 eventually will equal N_1 .

When the decay product of the original radionuclide is another radionuclide, three distinct equilibrium relationships exist between the parent and progeny based on the half-lives of the original and newly formed radionuclides. “Radioactive equilibrium” may be described mathematically by combining the decay-rate equations of two or more radionuclides to relate the number of atoms of one to any of the others. The three relationships between parent and progeny are referred to as “secular,” “transient,” and “no equilibrium” (Friedlander et al., 1981).

14A.1 Radioactive Equilibrium

A dynamic condition is initiated when a parent decays to a radioactive progeny. The progeny has its own decay equation, analogous to Equation 14A.1:

$$-\left(\frac{dN_2}{dt}\right) = \lambda_2 N_2 \quad (14A.2)$$

The relationships may become complicated if the progeny gives rise to an isotope that is also radioactive. In this case, the relationship would become, “parent–1st progeny–2nd progeny.” This connection of the radionuclides is referred to as a radioactive “decay chain.” When the parent of the chain is present, some number of atoms of all of the progeny in the chain eventually will be present as the predecessor radionuclides undergo radioactive decay.

14A.1.1 Secular Equilibrium

Secular equilibrium occurs when half-life of the progeny is much less than the half-life of the parent. An example, using the parent-progeny relationship between ^{210}Pb ($t_{1/2} \approx 22.6$ y) and ^{210}Bi ($t_{1/2} \approx 5$ d), can be used to demonstrate this case. (For illustrative purposes, ignore the radioactive progeny of the ^{210}Bi radionuclides).

Figure 14A.1 identifies the entire decay chain from ^{238}U , of which ^{210}Pb and ^{210}Bi are a part.

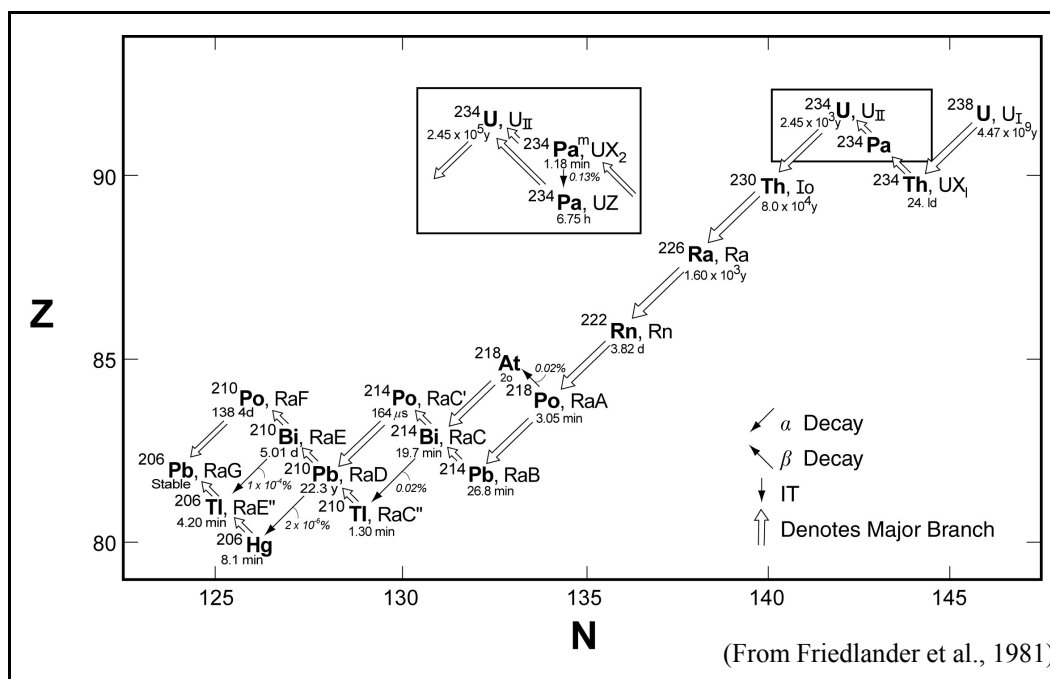


FIGURE 14A.1 — Decay chain for ^{238}U

When a group of atoms of lead are isolated (e.g., radiochemical purity is achieved by precipitation), no atoms of bismuth are present at the time of isolation ($t = 0$). From that moment, the number of atoms of bismuth present can be described by two equations: the rate of decay of the lead and the rate of decay of the bismuth. For each atom of lead that decays, one atom of bismuth is produced. Thus a single equation can be developed to show this relationship:

$$\text{Activity of } ^{210}\text{Bi} = \left[\frac{dN_2}{dt} \right] = \lambda_1 N_1 - \lambda_2 N_2 \quad (14A.3)$$

This equation can be solved to yield a relationship between the number of atoms of lead and bismuth at any time t after the isolation of lead. The general equation is:

$$N_2 = N_1^0 \left[\frac{\lambda_1}{(\lambda_2 - \lambda_1)} \right] \{ e^{-\lambda_1 t} - e^{-\lambda_2 t} \} + N_2^0 e^{-\lambda_2 t} \quad (14A.4)$$

Where: N_2 = atoms of progeny (bismuth), present at any time t
 N_1^0 = atoms of parent (lead), initially present
 λ_1 = decay constant of parent
 λ_2 = decay constant of progeny

N_2^0 = The number of atoms of progeny present at the time of isolation of parent.

The activity of the progeny (A_2) can then be calculated by multiplying both sides of Equation 14A.4 by λ_2 :

$$A_2 = \lambda_2 N_2 = N_1^0 [\lambda_2 \lambda_1 / (\lambda_2 - \lambda_1)] \{ e^{-\lambda_1 t} - e^{-\lambda_2 t} \} + \lambda_2 N_2^0 e^{-\lambda_2 t} \quad (14A.5)$$

If radiochemical purity is ensured initially, then

$$N_2^0 = 0 \quad (14A.6)$$

and the terms including N_2^0 in both Equations 14A.4 and 14A.5 equal zero.

Plotting this relationship as a function of time yields the graph shown in Figure 14A.2 for the ^{210}Pb - ^{210}Bi radionuclides. The three significant aspects of this relationship are:

- The total activity of the sample actually increases to a maximum (until it is $\approx 2A_{\text{pb}}$),
- The activity of the bismuth and lead are approximately equal after about seven times the half-life of bismuth, and
- The activity of bismuth decays with the half-life of lead after equilibrium has been established.

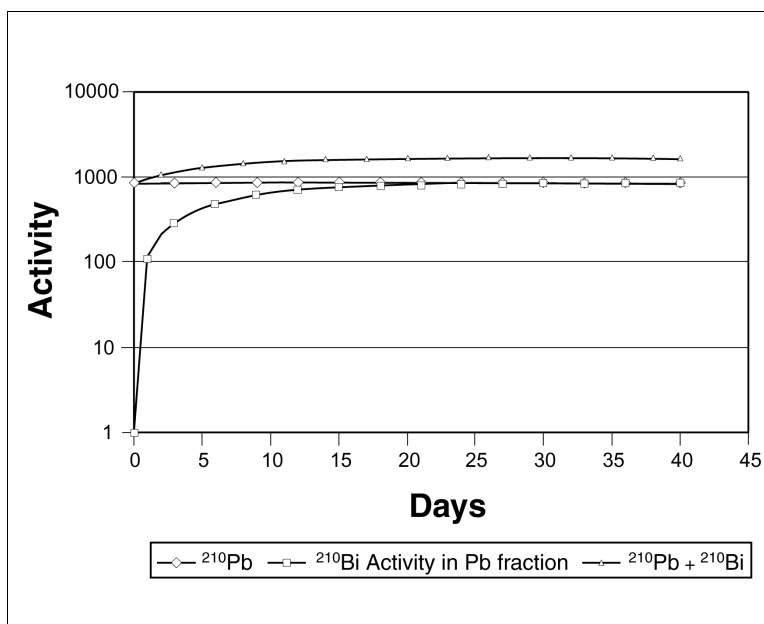


FIGURE 14A.2 — Secular equilibrium of $^{210}\text{Pb}/^{210}\text{Bi}$

14A.1.2 Transient Equilibrium

Transient equilibrium occurs when the half-life of the progeny is less than the half-life of the parent. This can be demonstrated using the relationship between ^{95}Zr ($t_{1/2} \approx 64$ d) and ^{95}Nb ($t_{1/2} \approx 35$ d). Figure 14A.3 identifies the same types of relationships as were seen in the case of secular equilibrium. For transient equilibrium, the total activity passes through a maximum, and then decreases with the characteristic half-life of zirconium. Note that the activity of the niobium exceeds the activity of the zirconium after about 2 half-lives of the niobium. A significant aspect

of this radioactive equilibrium that occurs at about this time is that the activity curve for the progeny reaches a maximum value. This can be determined for the general case by taking the first derivative of Equation 14A.5 and setting it equal to zero (Equation 14A.7):

$$A_{\text{maximum, progeny}} = \frac{[\lambda_1 - \lambda_2]}{[\ln \lambda_1 - \ln \lambda_2]} \quad (14A.7)$$

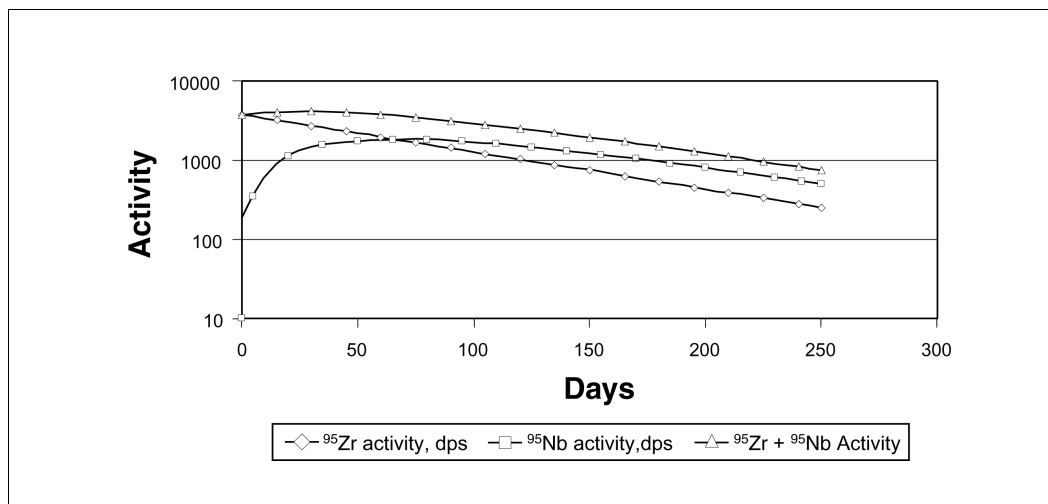


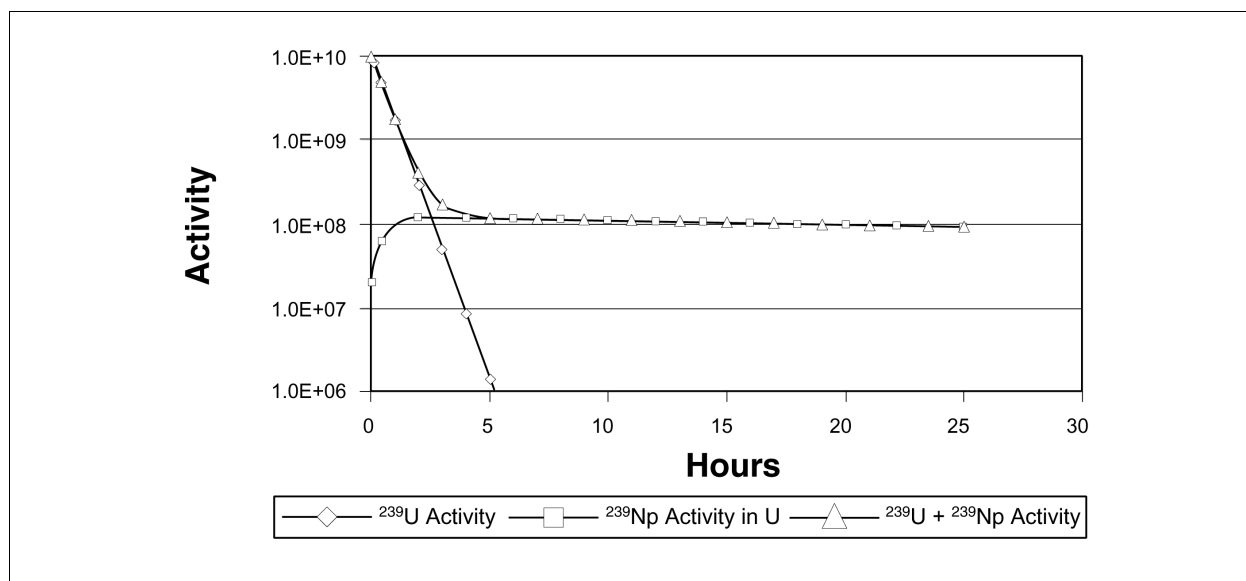
FIGURE 14A.3 — Transient equilibrium of ⁹⁵Zr/⁹⁵Nb

For the example in Figure 14A.3, this occurs at 67 days. When performing low-level analysis, knowing when this maximum activity occurs can help to achieve a lower minimum detectable amount of the progeny.

After approximately seven times the half-life of the progeny (in this case ⁹⁵Nb), the activity of the progeny decays with the half-life of the parent, similar to the secular equilibrium case. If the ⁹⁵Nb were to be separated from the parent at any time, it would decay with its own characteristic half-life.

14A.1.3 No Equilibrium

The no-equilibrium case occurs when the half-life of the progeny is greater than the half-life of the parent. Figure 14A.4 demonstrates this example for ²³⁹U ($t_{1/2} \approx 23.5$ min) and ²³⁹Np ($t_{1/2} \approx 2.36$ d $\approx 3,400$ min). The notable characteristic here is the total activity continually decreases after time zero.

FIGURE 14A.4 — No equilibrium of $^{239}\text{U}/^{239}\text{Np}$

14A.1.4 Summary of Radioactive Equilibria

In all three cases, Equation 14A.5 is used to calculate the activity of progeny after radiochemical separation of the parent. The important aspects of the relationship (Table 14A.1) are:

- It allows the analyst to optimize when, and for how long, to count a sample in which a parent-progeny relationship exists. For the secular and transient radiochemical equilibria, if approximately seven times the half-life of the progeny has passed, then equilibrium has been established. Thus for the $^{90}\text{Sr}/\text{Y}$ parent-progeny pair, the time to reach maximum activity is $\approx 7 \times (t_{1/2} \text{ Yttrium})$, or about 18 days.
- For the “transient equilibrium” case, a higher progeny activity may be achieved (relative to the parent), thus improving counting statistics for calculation of the initial parent activity.
- For the “no-equilibrium” case, if approximately seven times the half-life of the parent has passed, only progeny is left, and the activity of progeny can be related directly to the initial activity of the parent.
- It provides the analyst with important information about timing of intermediate separation steps in procedures (e.g., whether or not analysis must proceed immediately or can be set aside for a certain period of time).

TABLE 14A.1 — Relationships of radioactive equilibria

Type of Equilibrium	Relationship of Half-lives	Advantages	Other Useful Examples
Secular	Parent \gg Progeny	If progeny half-life is as short as a few days, equilibrium is established in a reasonable time frame for analysis.	$^{90}\text{Sr} - ^{90}\text{Y}$ $^{137}\text{Cs} - ^{137\text{m}}\text{Ba}$ $^{226}\text{Ra} - ^{222}\text{Rn}$ $^{228}\text{Ra} - ^{228}\text{Ac}$
Transient	Parent $>$ Progeny	If both half-lives are measured in hours to days, equilibrium activity of progeny peaks in a reasonable time frame for analysis.	^{222}Rn with its decay chain (for de-emanation analysis) $^{212}\text{Pb} - ^{212}\text{Bi}$
None	Parent $<$ Progeny	If parent half-life is a day or less, its activity contributes negligibly after a week.	$^{131}\text{Te} - ^{131}\text{I}$

14A.1.5 Supported and Unsupported Radioactive Equilibria

The connection between parent and progeny has one additional aspect that is significant for environmental analysis: whether or not the progeny activity is constantly “supported” by the parent in the sample. When the progeny is constantly supported, it appears to have the half-life of the parent. However, it can become unsupported, in which case it would decay with its own characteristic half-life.

For example, consider a soil sample that was contaminated with 3.7 Bq/g (100 pCi/g) of ^{232}Th ($t_{1/2} \approx .4 \times 10^{10}$ y). One concern about this radionuclide is the dissolution of some of its progeny into ground water: ^{228}Ra ($t_{1/2} \approx 5.76$ y), ^{224}Ra ($t_{1/2} \approx 3.66$ d) and ^{220}Ra ($t_{1/2} \approx 55.6$ s). Ground-water pH is normally between 6 and 8. At this pH, and with the crustal concentration of thorium/radium, the solubility of radium is significantly greater than that of thorium. As ^{228}Ra dissolves in the ground water, the ^{232}Th parent remains in the soil phase. The ground water will then migrate with the radium into wells, streams, aquifers, etc. The radium in the ground water is now “unsupported” because it is no longer in equilibrium with the decay of the thorium.

If we continue to follow the decay chain to ^{228}Th , the insolubility of thorium again “breaks” the decay chain in the ground water, because it will precipitate. However, its two progeny (^{224}Ra and ^{220}Rn) will continue to be soluble, and thus also be unsupported.

This is important when making decisions about sample shipment method and holding times prior to analytical separations. If it is assumed that the decay chain is supported, there is no reason to hasten the onset of the chemical analysis. However in the unsupported case, the half-lives of the ^{224}Ra and ^{220}Ra will affect the ability to achieve project measurement quality objectives and data quality objectives.

14A.2 Effects of Radioactive Equilibria on Measurement Uncertainty

14A.2.1 Issue

It is sometimes necessary to ensure that radionuclides have achieved radioactive equilibrium with their progeny or to establish and correct for disequilibrium conditions. This is particularly applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny, or long-lived progeny from their parents. This is also applicable for nondestructive assays like gamma spectrometry, where photon emission from progeny may be used to determine the concentration of a stable parent, or a parent which is radioactive but not a gamma emitter.

14A.2.2 Discussion

Application of Equations 14A.4, 14A.5, 14A.6 and 14A.7 can be shown by example. Radium-226 ($t_{1/2} \approx 1,600$ y), is a common, naturally occurring radionuclide in the uranium series. Radium-226 is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides beginning with the ^{222}Ra ($t_{1/2} \approx 3.8$ d) and ending with stable lead. As soon as ^{226}Ra is chemically separated from its progeny in an analytical procedure (via coprecipitation with barium sulfate), its progeny begin to re-accumulate. The progeny exhibit a variety of alpha, beta, and gamma emissions, some of which will be detected when the precipitate is counted. The activity due to the ingrowth of radon progeny should be considered when evaluating the counting data (Kirby, 1954). If analysis of radon is performed, the ingrowth of all progeny must be allowed prior to counting in order to minimize uncertainty. Examining the decay chain (Figure 14A.1) and the respective half-lives of radionuclides through ^{214}Po (for the purposes of the analysis, the progeny ^{214}Pb ends the decay chain and contributes insignificantly to the total count rate), it is appropriate to wait about 3 or 4 hours. In some cases, it may be necessary to derive correction factors for radioactive ingrowth and decay during the time the sample is counting. These factors are radionuclide-specific and should be evaluated for each analytical method.

Radioactive equilibrium concerns also apply to non destructive assays, particularly for uranium and thorium series radionuclides. Important radionuclides in these series (e.g., ^{238}U and ^{232}Th) have photon emissions that are weak or otherwise difficult to measure, while their shorter-lived primary, secondary or tertiary progeny are easily measured. This allows for the parents to be quantified indirectly—i.e., their concentration is determined by measuring their progeny and accounting for the length of time between separation of parent and progeny.

When several radionuclides from one decay chain are measured in a sample, observed activity ratios can be compared to those predicted by decay and ingrowth calculations, the history of the sample and other information. For example, undisturbed soil typically contains natural uranium with approximately equal activities of ^{238}U and ^{234}U , while water samples often have very different $^{238}\text{U}/^{234}\text{U}$ ratios. Data from analysis of ores or materials involved in processing that

could disrupt naturally occurring relationships (i.e., selectively remove elements from the material) require close attention in this regard.

All numerical methods (electronic and manual) should be evaluated to determine if the appropriate correction factors related to equilibrium concerns have been used. This includes a check of all constants used to derive such correction factors, as well as the use of input data that unambiguously state the time of all pertinent events (chemical separation and sample counting). A specific example is ^{228}Ra analysis with ingrowth of ^{228}Ac . The actinium is separated from the radium after a measured time and is immediately counted. The half-life of actinium is used to correct for the decay of actinium atoms during the counting interval and for the time interval since the separation from radium. Equation 14A.4 is used to calculate the atoms of radium, based on the number of atoms of actinium, at the time of separation of actinium from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection as follows:

$$N_B = N_c / [\epsilon] [1 - \text{EXP}(-\lambda_{\text{Ac}} t_c)]$$

and

$$N_0 = N_B \{ \text{EXP}(+\lambda_{\text{Ac}} t_s) \}$$

Where:

N_c is the number of counts accumulated during the counting interval

N_B is the number of atoms of actinium at the beginning instant of the count interval

N_0 is the number of atoms of actinium decay corrected back to the time of separation from Ra

λ_{Ac} is the decay constant for actinium

ϵ is the detector efficiency

t_c is the counting interval (clock time)

t_s is the time between separation of actinium from radium to the start of the count interval.

Equation 14A.4 is then used to calculate the atoms of radium based on the number of atoms of actinium that exist at the time actinium is separated from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection.

Samples requiring progeny ingrowth should be held for sufficient time before counting to establish equilibrium. Limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. For ingrowth, the limits should reflect the minimum time required to ensure that the radionuclide(s) of interest has accumulated sufficiently to not adversely affect the detection limit or uncertainty. Conversely, the time for radioactive decay of the radionuclides of interest should be limited such that the decay factor does not elevate the minimum detectible concentration or adversely affect the measurement uncertainty.

Samples where equilibrium is incorrectly assumed or calculated will produce data that do not represent the true sample concentrations. It is difficult to detect errors in equilibrium assumptions or calculations. Frequently, it takes anomalous or unanticipated results to identify these errors. In these cases, analysts need to know the sample history or characteristics before equilibrium errors can be identified and corrected. Some samples may not be amenable to nondestructive assays because their equilibrium status cannot be determined; in such cases, other analytical methods are indicated.

14A.2.3 Examples of Isotopic Distribution – Natural, Enriched, and Depleted Uranium

Isotopic distribution is particularly important with respect to uranium, which is ubiquitous in soils and is also a contaminant in many site cleanups. The three predominant uranium isotopes of interest are ^{238}U , ^{234}U , and ^{235}U , which constitute 99.2745, 0.0055, and 0.72 atom-percent, respectively, of natural uranium², i.e., uranium as found in nature (Parrington et al., 1996). The ratio of ^{238}U to ^{234}U in undisturbed uranium deposits will be the same as the ratio of $99.2745/0.0055 = 18,050$, because all the ^{234}U comes from the decay of ^{238}U (^{234}U originally present when the Earth was formed has long since decayed).

However, human activities related to uranium typically involve changing the ratio of natural uranium by separating the more readily fissionable ^{235}U from natural uranium to produce material “enriched” in ^{235}U , for use in fuel cycle and nuclear weapons related activities. Typical ^{235}U enrichments range from 2 percent for reactor fuels to greater than 90 percent ^{235}U for weapons. The enrichment process produces material that is called “DU,” or depleted in uranium (i.e., the uranium from which the ^{235}U was taken³). The enrichment process also will disrupt the ^{234}U content, which will change the $^{238}/^{234}\text{U}$ ratio from what is occurring naturally (i.e., 18,050). While the ^{235}U concentrations of depleted uranium are reduced relative to natural ores, they still can be measured by several assay techniques. This gives rise to uranium with three distinct distributions of ^{238}U , ^{235}U , and ^{234}U , referred to as “natural,” “enriched,” and “depleted” uranium. Because ^{238}U , ^{235}U , and ^{234}U are alpha emitters with considerably different half-lives and specific activity, a measurement of a sample’s total uranium alpha activity cannot be used to quantify the sample’s isotopic composition or uranium mass without knowing if the uranium is natural or has been enriched or depleted in ^{235}U . However, if this information is known, measurement and distribution of the sample’s uranium alpha activity can be used to infer values for a sample’s uranium mass and for the activities of the isotopes ^{238}U , ^{235}U , and ^{234}U . This ratio can be determined directly or empirically using mass or alpha spectrometry, techniques that are time- and cost-intensive, but which provide the material’s definitive isotopic distribution. It is often

² The natural abundance of ^{235}U of 0.72 atom-percent is a commonly accepted average. Actual values from specific ore samples vary.

³ Enriched and depleted refer primarily to ^{235}U .

practical to perform mass or alpha spectrometry on representative samples from a site to establish the material's isotopic distribution, assuming all samples from a given area are comparable in this respect. Once established, this ratio can be applied to measurements of uranium alpha activity to derive activity concentrations for ^{238}U , ^{234}U , and ^{235}U data.

14A.3 References

- Friedlander, G., Kennedy, J.W., Macias, E.S., and Miller, J.M. 1981. *Nuclear and Radiochemistry*, John Wiley and Sons, New York.
- Kirby, H.W. 1954. "Decay and Growth Tables for the Naturally Occurring Radioactive Series." *Anal. Chem.* 26:6, p. 1063-1071.
- Parrington, J.R., Knox, H.D., Breneman, S.L., Feiner, F., and Baum, E.M. 1996. *Nuclides and Isotopes: Chart of the Nuclides*. 15th Edition. Lockheed Martin and General Electric.